

ELECTROCHEMICAL MODIFICATIONS IN KAOLINITE–GLASS BEAD PLUGS.

MINERALOGICAL AND PHYSICO–CHEMICAL MODIFICATIONS

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Abstract – Electrochemical treatment of kaolinite–glass bead plugs in the presence of water and CaCl_2 solutions produces dissolution of the glass beads, corrosion of the anodes, and transport of the released elements toward the cathodic zone. In this area, new mineral phases (both amorphous and crystalline) are synthesized. Most of these new phases, and especially the calcium silicate hydrate (CSH-1), are well known to exhibit important cementing properties. The nature and the extent of the modifications brought about by the treatment are dependent on the nature of the electrodes, the pH and the ionic strength of the circulating electrolyte, and the duration of the treatment.

INTRODUCTION

THE STABILIZATION of loose or cohesionless soils by electrochemical treatment is to-day a conventional method. Casagrande (1930) is the pioneer in this field. He found that when an electric current is passed into clay soils via metal electrodes (aluminum and copper), a marked strengthening is observed and some of the soils become unwettable. Furthermore, he reported that the extent of the strengthened areas varies with the current strength, electrode shape and distance between the electrodes.

Electrochemical treatment provokes various chemical processes, which include solution, oxidation reduction, and hydrolysis accompanied by physico–chemical processes such as temperature change, electro–osmosis, electrophoresis, pore size decrease, coagulation, crystallization, sorption and change in sorption capacity, exchange reaction, migration of electrolytes, formation of large dipoles, orientation of clay particles and changes in the mechanical strength of the treated samples.

The main purpose of the present investigation was to evaluate electrochemically-induced modifications in the mineralogical, chemical, physical and mechanical properties of kaolinite–glass bead plugs. Only the changes in mineralogical and physico–chemical properties will be discussed in this paper. Objectives of the study were to examine the role of electrode material (carbon, aluminum and iron) and of electrolyte pH in influencing the extent of the above-mentioned modifications.

EXPERIMENTAL PROCEDURE

Description of the starting materials

Artificial soils were prepared by blending 50:50 mixtures of kaolinite and glass beads, and 49:49:2 mixtures of kaolinite–glass beads and amorphous ferric hydroxide respectively.

The kaolinite was supplied by “Le Kaolin Breton” and was found to be without any appreciable impurities. This kaolinite was well crystallized, with a specific surface area of $13.8 \text{ m}^2\text{g}^{-1}$. It was saturated with N/10 CaCl_2 and was used as such without further fractionation.

Glass beads were supplied by Glaverbel, Belgium and were fractionated by sedimentation in water. Particles having less than $10 \mu\text{m}$ equivalent Stokes dia. were used in the experiments. The powder had a specific surface area of $2.38 \text{ m}^2\text{g}^{-1}$ and was amorphous in nature.

Amorphous ferric hydroxide was prepared by precipitating N/10 FeCl_3 solution with 1 N NaOH at pH 8.0, followed by dialysis for 10 days and then dried by freeze-drying. The chemical formula of this hydroxide was $\text{Fe}_2\text{O}_3 \cdot 1.57 \text{ H}_2\text{O}$ and its specific surface area was $272.50 \text{ m}^2\text{g}^{-1}$.

Why kaolinite as a starting material

According to Grim (1968), kaolinite does not undergo any appreciable change when submitted to electrochemical treatment. It does not swell like montmorillonite, so the permeability or pore-size-distribution does not change much, provided nothing else is added externally. Moreover, since it acts as an insulator and does not conduct electricity

internally, the data on its electrophoretic behavior is more reliable than that for montmorillonite (Marshall, 1964). It is clear from these properties that kaolinite should represent the simplest model for examination of the changes produced by electrochemical treatment.

Preparation of starting materials

A given sample was thoroughly mixed with distilled water overnight with a magnetic stirrer. The mixture was then dried slowly at 70°C while being stirred in order to get a homogeneous sample. Heating was continued until the sample had a stiff consistency and a water content near the plastic limit. This paste was remolded and compressed to an undrained confined pressure of 50 kg cm⁻². The sample was put in the molder in small portions each time and then compressed in order to get the maximum homogeneity possible. The blocks so obtained were dried by a current of hot air and were used for the experiments with no other pretreatment.

For some experiments (numbers 14–19), partially dried mixtures with a stiff consistency were put directly into a perforated tube of Plexiglas with an internal diameter and length of 15 cm (made by joining three identical pieces of plexiglas, each 5 cm long), and then compacted slightly by hand.

Electrolytic cell and electrochemical treatment

The electrical circuit employed is commonly used in coulometric analysis which functions at

constant potential difference, but varying current density. The electrochemical treatment consisted of simultaneously circulating an electrolytic solution around and passing a direct current through the clay block (Fig. 1).

Rieke *et al.* (1966) emphasized that the efficiency of the system is reduced as drainage proceeds due to electrochemical treatment. This reduction is explicable by increased electrical resistance, reduced water mobility and back suction gradients. Therefore, in order to increase the efficiency of the electrochemical treatment, the solution was circulated continuously outside the clay plug during the electrochemical treatment. The plugs were of 3.5 cm length and 3.1 cm dia. for experiments 1–13 and of 15 cm length and 2.1 cm dia. for experiments 14–19. They were put in a Plexiglas perforated cylinder in order to keep their original shape. The electrodes were brought into close contact with the sample on both sides of the cell.

The blocks were pore-filled with their circulating solution overnight, after which the current was turned on. The current density was recorded periodically. The detailed plan of the experiments is given in Table 1.

At the end of the experiment, the current was cut off and the blocks allowed to remain undisturbed for 3 days. They were then dried by a current of hot air, and cut into three approximately equal parts representing the anodic, central and cathodic zones (termed part *a*, part *m* and part *c*, respectively). Finally, these samples were oven dried

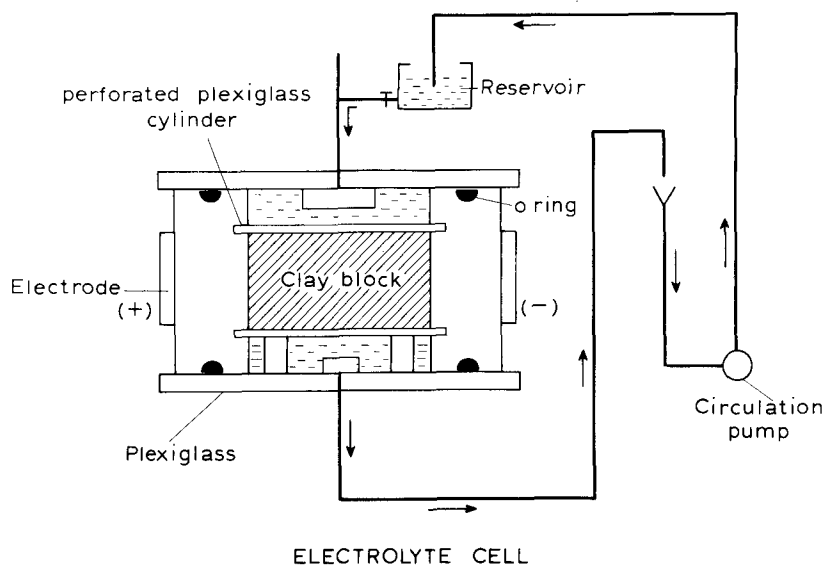


Fig. 1. Schematic diagram of electrolytic cell and flow of electrolytic solution.

Table 1. List of experiments performed

Experiment No.	Kaolinite (%)	Composition of blocks Glass beads (%)	$\text{Fe}_2\text{O}_3 \cdot 1.57\text{H}_2\text{O}$ (%)	Solution	Composition of circulating liquid pH	Electrode material	Length of block (cm)	Duration of electro-chemical treatment (hr)	$\Delta V/\Delta l$ (potential gradient, $\text{V} (\text{cm}^{-1})$)
1 C ₁₀	49	49	2	CaCl ₂	10.5	C	3.5	25	7.0
2 C ₈	49	49	2	H ₂ O	6.0	C	3.5	25	7.0
3 C ₄	49	49	2	CaCl ₂	4.0	C	3.5	25	7.0
4 C ₁₀	50	50		CaCl ₂	10.5	C	3.5	25	7.0
5 C ₈	50	50		H ₂ O	6.0	C	3.5	25	7.0
6 C ₄	50	50		CaCl ₂	4.0	C	3.5	25	7.0
7 Fe ₁₀	50	50		CaCl ₂	10.5	Fe	3.5	25	7.0
8 Fe ₈	50	50		H ₂ O	6.0	Fe	3.5	25	7.0
9 Fe ₄	50	50		CaCl ₂	4.0	Fe	3.5	25	7.0
10 Al ₁₀	50	50		CaCl ₂	10.5	Al	3.5	25	7.0
11 Al ₈	50	50		H ₂ O	6.0	Al	3.5	25	7.0
12 Al ₄	50	50		CaCl ₂	4.0	Al	3.5	25	7.0
13 C ₁₀	50	50		CaCl ₂	10.5	C	3.5	240	7.0
14 C ₁₀	50	50		CaCl ₂	10.5	C	15.0	75	2.4
15 C ₄	50	50		CaCl ₂	4.0	C	15.0	75	2.4
16 Fe ₁₀	50	50		CaCl ₂	10.5	Fe	15.0	75	2.4
17 Fe ₄	50	50		CaCl ₂	4.0	Fe	15.0	75	2.4
18 Al ₁₀	50	50		CaCl ₂	10.5	Al	15.0	75	2.4
19 Al ₄	50	50		CaCl ₂	4.0	Al	15.0	75	2.4

at 105°C. Experiments 1–12 were conducted in duplicate; one run was used to determine the modifications in pore-size distribution, the other for the remaining properties to be studied. Experiments 14–19 studied the modifications in mechanical properties of the kaolinite and glass bead mixtures.

The experimental conditions and electrolytes were chosen in such a way that in some experiments performed with pure water the electro-osmotic transport would be high (see Gray and Mitchell, 1967), but low in other experiments with 0.1 N CaCl_2 at pH of 10.5 and 4.0.

METHODS OF EXAMINATION OF TREATED SAMPLES

Instrumentation

An AEI EM6G electron microscope with an accelerating potential of 60 kV was used for bright field transmission microscopy. Ultrasonic vibration treatment was not used in order to avoid violent disruptions.

The X-ray examination of the crystalline compounds formed was carried out on a Philips diffractometer using nickel filtered $\text{CuK}\alpha$ radiation, by the standard random orientation powder mount technique. The crystallinity index for kaolinite was measured by the method of Hinckley (1963). B.E.T. surface area measurements were performed by a dynamic flow method (Cahen *et al.*, 1965) with N_2 gas as the adsorbate.

Chemical analysis

For both sample-water (1:2.5) suspensions and the leachate from 1 g of the sample treated with 100 ml of 1 N NH_4NO_3 , the pH was measured with a glass electrode. The total amount of soluble CaO in the leachate was determined by atomic absorption spectroscopy. The soluble SiO_2 in the leachate was measured colorimetrically after reducing silicomolybdc complex (Voinovitch *et al.*, 1962).

Total Al in a given sample was determined by a gravimetric method after precipitation by oxine in the presence of a complexing solution of KCN, E.D.T.A. and NH_4OH . Total iron content in some samples, present in the starting material or coming from anodic dissolution, was determined colorimetrically by the sulphosalicylic method (Voinovitch *et al.*, 1962).

RESULTS AND DISCUSSION

New crystalline phases

The new phases identified by X-ray diffraction were generally observed on the outside of the clay block near the cathode, except in experiments 1 C_{10} , 4 C_{10} where traces of $\text{Ca}(\text{OH})_2$ were found

in the cathodic zone of the clay block itself. Similarly, in experiments 10 Al_{10} and 12 Al_4 bayerite was observed at the extreme end of the clay block towards the cathode.

Of the minerals formed outside the clay block near the cathode, pure $\text{Ca}(\text{OH})_2$ was observed in experiment 7 Fe_{10} and $\text{Ca}(\text{OH})_2$ with some traces of calcite in experiment 9 Fe_4 . Pure calcite was formed in experiments 3 C_4 , 6 C_4 and 13 C_{10} , and along with traces of $\text{Ca}(\text{OH})_2$ was observed in experiments 1 C_{10} and 4 C_{10} . Therefore, it appears that the electrode material, starting pH and time for which current is passed play an important role in the carbonate-forming process.

While using Al electrodes with CaCl_2 as circulating solution, after 4–5 hr of the treatment a white product was deposited on the cathode, which was identified by X-ray diffraction as a mixture of calcium aluminium oxide hydrate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) and calcium aluminium hydroxide carbonate ($\text{Ca}_{16}\text{Al}_8(\text{OH})_{54}\text{CO}_3 \cdot 21 \text{H}_2\text{O}$) with traces of metallic aluminum and bayerite. On heating at 1000°C, this mixture was transformed to a calcium aluminate 12:7 ($12\text{CaO} \cdot 7 \text{Al}_2\text{O}_3 \cdot 0-1 \text{H}_2\text{O}$). This formula is in agreement with the chemical composition of the mixture heated at 105°C, i.e. $\text{Ca}_{12}\text{Al}_{14}(\text{OH})_{61-6}\text{Cl}_4(\text{CO}_3)_{0.4}10\text{H}_2\text{O}$.

All these observed crystalline phases are known to have cementing power. However, they could not be detected in the clay block because of either low concentration or entrapment by the hydrated calcium silicate. This possibility will be discussed later on.

New amorphous phases

Amorphous material was observed by electron microscopy only in the central or cathodic zone of experiment 13 C_{10} , mainly in the cathodic zone and not at all in the anodic zone. This product is shown in Fig. 3 and is composed of either thin fibres or foil-like material. Based on the classification of Diamond *et al.* (1964), the material was identified as amorphous calcium silicate hydrate, more precisely CSH-1.

Figure 4 shows agglomeration of hexagonal plates and deposition of CSH-1 around the kaolinite particles, the angles and edges of which are ill-defined. The formation of CSH-1 was also observed in the cathodic zone even when the current was passed for 1 day, provided that CaCl_2 was circulated during the experiment and C or Fe electrodes were used.

In experiment 7 Fe_{10} , the sorption of iron hydroxide sol, arising from anodic dissolution was

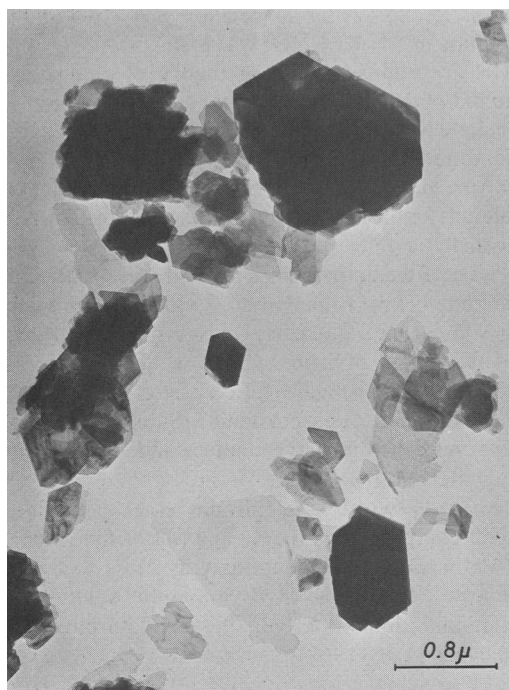


Fig. 2. Electron micrograph, experiment 13. anodic zone. Kaolinite with well defined angles and edges. Practically no change after 10 days of treatment.

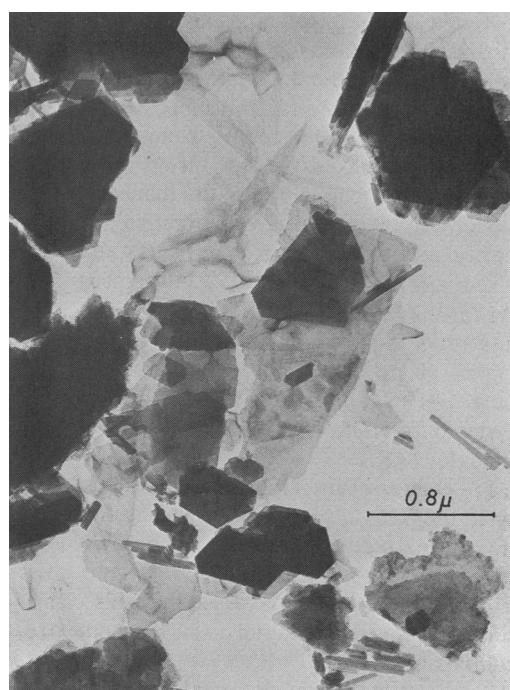


Fig. 3. Electron micrograph, experiment 13 central zone. Minute deposition on kaolinite edges and the presence of some foils and many thin platy fibres which are hydrated calcium silicate, amorphous to X-ray diffraction.

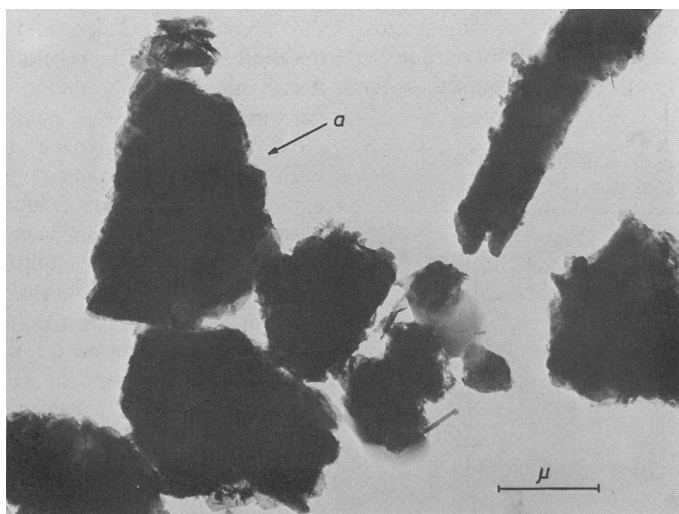


Fig. 4. Electron micrograph, experiment 13 cathodic zone—Agglomeration of kaolinite plates and deposition of amorphous material around the kaolinite particles.

observed on the edges and planes of all kaolinite particles in the anodic zone. In the same experiment, some of the kaolinite particles were left uncoated in the central zone, because of laminar flow of iron hydroxide coming from anodic dissolution. In these cases, the amount of iron hydroxide present is probably not more than the sorptive capacity of the kaolinite. No effective iron hydroxide bridge between kaolinite particles was observed.

Kaolinite crystallinity

In order to probe more deeply into the morphological changes observed in the cathodic zone, the degree of kaolinite crystallinity was followed by X-ray diffraction. The method used was that of Hinckley (1963).

The values of the Hinckley Index for crystallinity of the treated samples (only when C electrodes are used) are given on Table 2. These values vary from 0.97 to 1.34, whereas the variation given by Hinckley was 0.25–1.50. Based on this classification, the starting material as well as the treated samples belong to a category of soft kaolinite. The analysis of variance shows statistically that the treatment has no significant effect on the kaolinite crystallinity. Thus, the morphological differences observed in electron microscopy are independent of kaolinite crystallinity and are mainly caused by the accumulation of amorphous materials on the surfaces of kaolinite particles. These results suggest that kaolinite is not altered and does not participate in the production of the free silica required for the formation of CSH-1.

Table 2. Hinckley crystallinity index of the treated samples (only for the C electrodes)

Experiment No.	Anodic <i>a</i>	Zone Central <i>m</i>	Cathodic <i>c</i>
1C ₁₀	1.23	0.97	1.05
2C ₆	1.19	1.17	1.27
3C ₄	1.19	1.19	1.21
4C ₁₀	1.16	1.20	1.34
5C ₆	1.18	1.13	1.30
6C ₄	1.33	1.14	1.29
Starting material (50:50)		1.16	

C.V. = 7.39 per cent.
t = 1.45 N.S.

Changes in pH

Only the main features of the pH measurements are given. The pH of the starting material (50:50)

for 1:2.5 clay-water suspension was 11.05 and for leachate in 1 N NH₄NO₃ was 6.80.

In accordance with the theory of electrolysis, the pH of the 1:2.5 clay water suspension or of the leachate with 1 N NH₄NO₃ is higher in the cathodic zone and lower in the anodic zone than in the starting material. But the difference in magnitude depends entirely on the electrode material and the electrolytic pH.

When Fe electrodes are used, the pH in the anodic zone is lower than when C electrodes are used. This lowering is due partly to electrolysis and partly to hydrolysis of iron hydroxide. The hydrolysis reaction leads to the liberation of protons by olation and oxalation (Giessen, 1968). Similar results are observed when iron hydroxide is added to the starting material.

The pH with Al electrodes does not change much compared to others. The pH of the leachate is 6.8 in all the zones, and is very close to the isoelectric point or point of minimum solubility of aluminum ions (pH 6.70), as determined by Reesman *et al.* (1969).

Changes in soluble calcium and silica

In order to localize and to estimate the importance of the silica and calcium accumulation caused by the electrochemical treatment, the samples were leached with a 1 N NH₄NO₃ (pH 4.7) solution and the amounts of silica and calcium solubilized determined. From the results presented in Table 3, it is evident that, in general, the amounts of both calcium and silica were much higher in the cathodic zone and depleted in the anodic zone. Therefore, both calcium and silica migrated from anode to cathode. However, when aluminum electrodes were used, the same behavior was not observed and the same concentration of soluble calcium and silica was measured throughout the clay block.

From a qualitative viewpoint, Table 3 also shows that the molecular ratio CaO/SiO₂ obtained in any part of a given plug was strongly dependent on several parameters: nature of the electrodes, ionic strength and pH of the circulating solution, and duration of the treatment. Considering the usual CaO/SiO₂ molecular ratio in CSH-1 which, according to Taylor (1968), may vary from 0.8 to 1.5, it is clear that most of the calcium silicates which accumulated in the cathodic region were too rich in calcium. Therefore, high Ca products, like Ca(OH)₂ or CaCO₃, were probably entrapped within the clay matrix.

The solubilization study also provided some information about the source of the silica required

Table 3. Solubility of CaO and SiO₂ in 1 N NH₄NO₃ (pH 4.7), in moles per 100 g of sample

Experiment No.	Soluble CaO Zone			Soluble SiO ₂ Zone		
	<i>a</i>	<i>m</i>	<i>c</i>	<i>a</i>	<i>m</i>	<i>c</i>
1C ₁₀	1.23	24.50	42.0	0.49	4.43	8.87
2C ₈	0.77	1.05	28.70	0.49	0.82	6.40
3C ₄	0.88	15.40	37.80	0.49	2.55	6.24
4C ₁₀	2.00	17.50	34.30	0.82	2.63	4.43
5C ₈	1.12	6.30	17.50	1.56	6.24	13.03
6C ₄	1.21	15.40	27.30	0.82	2.63	3.53
7Fe ₁₀	5.60	11.90	35.70	2.74	5.75	13.96
8Fe ₆	3.47	8.40	16.80	3.28	11.49	18.71
9Fe ₄	6.51	13.30	21.35	4.43	11.08	14.37
10Al ₁₀	11.83	14.91	16.80	2.79	2.14	2.99
11Al ₆	9.24	7.70	7.70	12.81	11.99	11.99
12Al ₄	16.45	18.55	13.65	2.55	1.72	2.81
13C ₁₀	1.87	2.28	6.93	3.28	11.49	18.70
Starting material (50:50)		9.80			6.40	

for the formation of CSH-1. Using Peerless kaolinite in 1 N NH₄CL solution at pH 4.7, Low and Black (1947) reported the equilibrium concentration of SiO₂ to be 2.0×10^{-4} M. In the present study, the concentration of SiO₂ in the leachate of the starting material was found to be 6.4×10^{-4} M. Clearly, the kaolinite cannot be the source of such a high concentration of soluble silica. On the contrary, the kaolinite solubility should be suppressed due to the common ion effect. Therefore, the glass beads are assumed to be the main source of the free silica.

Movement of kaolinite particles from cathode to anode

Although our aim was not to measure the electrophoretic velocity, the total Al content in the samples after treatment gave evidence for the transport of kaolinite from cathode to anode.

The major source of Al in our system was kaolinite which contained 37.5 per cent Al₂O₃, the glass beads only 1 per cent. In general, the difference in kaolinite content between anodic and cathodic zones was 2–4 per cent, except when Al electrodes were used. In this case the Al content was almost the same in all zones; however, aluminum was also provided by electrode corrosion.

Sethi (1973) has observed that such small differences in kaolinite content, particularly when the overall concentration was so high, do not influence the physical and mechanical properties of the matrix. Therefore, in this study such differences are small enough to be ignored.

Movement of iron hydroxide added in the starting material during electrolysis

The amorphous Fe₂O₃ · 1.57 H₂O, prepared at pH 8.0 near the iso-electric point (i.e.p.), was added to the starting material of experiments 1–3. After the electrochemical treatment Fe₂O₃ was concentrated in the central zone when CaCl₂ and in the cathodic zone when H₂O was used as the circulating liquid (Table 4).

Table 4. Total Fe₂O₃ content in the samples (1.7 per cent Fe₂O₃ or 2 per cent Fe₂O₃ · 1.57 H₂O was added to the starting material), showing the movement during electrolysis

Experiment No.	Zones		
	<i>a</i>	<i>m</i>	<i>c</i>
1 C ₁₀	1.45 (206.90)*	1.78 (382.02)	1.67 (76.05)
2 C ₈	1.60 (340.00)	1.63 (423.31)	2.12 (603.30)
3 C ₄	1.60 (189.38)	1.85 (338.92)	1.64 (135.98)

*The data in brackets indicates the surface area of Fe₂O₃ alone as calculated by the difference in surface area of the samples with and without adding Fe₂O₃ while using C electrodes.

This difference suggests that there was a change in the surface charge of Fe₂O₃ which was related to a change in pH during electrolysis. With CaCl₂, the current density was quite high, and therefore the rate of electrolysis was high. The pH at the cathodic zone went above the i.e.p., pH 8.5 (Parks

and de Bruyn, 1962), and below the i.e.p. at the anodic zone. Iron hydroxide thus acquired a positive charge in the anodic zone and a negative charge in the cathodic zone and therefore moved from both sides toward the center.

With H_2O as the circulating fluid, the pH of the iron hydroxide was probably always below the i.e.p. because of the low current density. Therefore, a net movement of iron oxide from anode to cathode was observed. Furthermore, only the smaller particles moved during the electrochemical treatment, which is evident from the calculated values of the specific surface area reported in brackets in Table 4.

Specific surface area (B.E.T. method)

The data in Table 5 show the changes in specific surface areas of different zones of the clay plug and the influence of the electrolytic solution, its starting pH and the electrodes used.

Table 5. Specific surface area determined from B.E.T. dynamic method (m^2/g)

Experiment No.	S_0 , B.E.T. Zone		
	<i>a</i>	<i>m</i>	<i>c</i>
1 C_{10}	12.00	17.64	16.58
2 C_6	14.20	17.80	23.74
3 C_4	10.12	15.54	17.10
4 C_{10}	9.00	10.84	15.31
5 C_6	8.76	10.90	10.95
6 C_4	7.09	9.27	14.87
7 Fe_{10}	28.90	43.30	28.20
8 Fe_6	37.06	34.91	20.44
9 Fe_4	28.47	26.47	16.44
10 Al_{10}	8.30	7.89	7.83
11 Al_6	24.31	12.51	11.68
12 Al_4	9.53	8.06	7.12
13 C_{10}	21.48	54.02	62.77
Starting material 50:50		8.70	

A gradual increase in S_0 was observed from the anodic to the cathodic zone in the case of carbon electrodes. Since there was an insignificant corrosion of the carbon electrodes, this increase was mainly due to the accumulation of the amorphous calcium silicate (CSH-1). The surface area of a pure sample of CSH-1 may vary from 135 to about $380 m^2 g^{-1}$ (Brunauer and Greenberg, 1962), and a similar range has been reported for CSH (gel) materials. The difference in anodic and cathodic regions became more pronounced when the time of

passage of the current is increased to 10 days (experiment 13 C_{10}).

The surface area is relatively higher in all portions when some iron oxides are added and when Fe electrodes are used. This increase is relatively higher in the cathodic region, where an iron accumulation is observed.

With Al electrodes, the behavior of S_0 was quite different from the other experiments. With 0.1 N $CaCl_2$ as the circulating electrolyte, there was practically no increase in the specific surface area. However, when water was used as the circulating liquid, an appreciable increase in surface area was observed in the anodic part. In this case, the amount of soluble SiO_2 was higher (Table 3) than in the other experiments while the soluble CaO remained practically the same as in the starting material. This behavior suggests the formation of amorphous silica or silico-alumina, which caused the increase in the specific surface area.

CONCLUSION

During electrochemical treatment of kaolinite and glass bead mixtures in the presence of $CaCl_2$ or water as circulating liquid, the formation of cementing agents, either crystalline or amorphous, was observed, mainly in the cathodic zone. These agents were calcite, $Ca(OH)_2$, and a mixture of hydrated calcium aluminate outside the clay block and amorphous hydrated iron oxide, and CSH-1 inside the clay block.

Although the general trend was the accumulation of CSH-1 in the cathodic zone, the results show the strong interaction of factors such as the nature of the electrodes and the time of treatment. The cementing properties of amorphous hydrated calcium silicate (CSH-1) increased the mechanical strength of the matrix. This aspect will be discussed in a future paper.

Also noteworthy is the observation that the kaolinite itself does not seem affected by the electrochemical treatments.

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Résumé— Le traitement électrochimique de blocs comprimés de kaolinite et de billes de verre en présence d'eau et de solution de CaCl_2 , entraîne une dissolution des billes de verre, une corrosion des anodes et le transport des éléments libérés vers la zone cathodique. Dans cette zone, des phases minérales nouvelles (amorphes et cristallisées) sont synthétisées. La plupart de ces phases nouvelles, et notamment le silicate de calcium hydraté (CSH-1) sont bien connues pour leurs propriétés de ciment.

La nature et l'intensité des modifications apportées par le traitement dépendent de la nature des électrodes, du pH et de la force ionique de l'électrolyte circulant et de la durée du traitement.

Kurzreferat— Die elektrochemische Behandlung von Kaolinit-Glasperlen-Preßlingen in Gegenwart von Wasser und CaCl_2 -Lösungen ruft Lösung der Glasperlen, Korrosion der Anoden und den Transport der freigesetzten Elemente in Richtung auf die Kathodenzone hervor. In diesem Bereich werden neue Mineralphasen (sowohl amorphe als auch kristalline) gebildet. Die meisten dieser neuen Phasen und besonders das Calcium-silikathydrat (CSH-1) weisen bekanntlich wichtige zementierende Eigenschaften auf.

Die Natur und das Ausmaß der durch die Behandlung hervorgerufenen Umwandlungen hängt von der Art der Elektroden, dem pH-Wert und der Ionenstärke der umlaufenden Elektrolytlösung, sowie von der Dauer der Behandlung ab.

Резюме — Электрохимическая обработка каолинита и «пуговок» бисеров стекла в растворе воды и CaCl_2 повела к растворению бисеров стекла, к коррозии анодов, и к переносу освобожденных элементов в катодную зону. В этой сфере исследования синтезируются новые фации минералов (как аморфных, так и кристаллических). Большинство этих новых фаций, особенно гидроксид силиката кальция (CSH-1), как хорошо известно, проявляют склеивающую способность. Характер и степень изменений возникающих вследствие обработки зависят от свойств электродов, от pH, от ионной силы кругового движения электролита и от продолжительности обработки.